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First Inventor or Application Identifier		Wakako MORIYAMA, et al.
Title	METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICES USING THERMAL NITRIDE FILMS AS GATE INSULATING FILMS	

<b>APPLICATION ELEMENTS</b> See MPEP chapter 600 concerning utility patent application contents	<b>ADDRESS TO:</b> Assistant Commissioner for Patents Box Patent Application Washington, DC 20231
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5. <input type="checkbox"/> Incorporation By Reference (usable if box 4B is checked) The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4B, is considered to be part of the disclosure of the accompanying application and is hereby incorporated by reference therein.	12. <input type="checkbox"/> Small Entity Statement(s) <input type="checkbox"/> Statement filed in prior application, Status still proper and desired.
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<input type="checkbox"/> Continuation <input type="checkbox"/> Divisional <input type="checkbox"/> Continuation-in-part (CIP) of prior application no.:	14. <input checked="" type="checkbox"/> Other: Notice of Priority, List of Inventors' Names and Addresses, List of Related Cases, Statement of Relevancy
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TITLE OF THE INVENTION

METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICES USING  
THERMAL NITRIDE FILMS AS GATE INSULATING FILMS

CROSS-REFERENCE TO RELATED APPLICATIONS

5           This application is based upon and claims the  
benefit of priority from the prior Japanese Patent  
Application No. 11-272322, filed September 27, 1999,  
the entire contents of which are incorporated herein by  
reference.

10           BACKGROUND OF THE INVENTION

          This invention relates to a method for  
manufacturing semiconductor devices such as nonvolatile  
memories or MOS transistors using thermal nitride films  
as gate insulating films and more particularly to a  
15       method for manufacturing cell transistors of a NAND  
cell type EEPROM (Electrically Erasable and  
Programmable Read-Only Memory).

          FIG. 1 is a pattern plan view showing the memory  
cell structure of a NAND cell type EEPROM (NAND cell  
20       type flash memory) and FIG. 2 shows the equivalent  
circuit thereof. As shown in FIGS. 1 and 2, the  
current paths of a plurality of cell transistors CG1 to  
CGn which are each formed of an n-channel MOSFET having  
a stacked gate structure including a floating gate and  
25       control gate are serially connected. The drain of the  
cell transistor CG1 which is disposed on one end side  
of the current paths is connected to a bit line BLi

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(i = 1, 2, ...) via the current path of a selection n-channel MOS transistor Q1 and the source of the cell transistor CGn which is disposed on the other end side of the current paths is connected to a source line (ground potential) SL via the current path of a selection n-channel MOS transistor Q2. The transistors CG1 to CGn, Q1, Q2 are formed in the same well region. The control gates of the cell transistors CG1 to CGn are connected to word lines WL1 to WLn which are each continuously formed in the row direction and the gates of the selection transistors Q1, Q2 are respectively connected to selection lines SG1, SG2. Further, one-side ends of the respective word lines WL1 to WLn are connected to connection pads for connection with a peripheral circuit via Al wirings. The connection pads are formed on an element isolation region.

Next, the outline of the manufacturing method of the cell transistors of the NAND cell type flash memory is explained with reference to FIGS. 3A to 3G corresponding to a cross section taken along the 3-3 line of the pattern plan view of FIG. 1.

First, a silicon oxide film 2 with a film thickness of 7 nm is formed on a silicon substrate 1 by use of the thermal oxidation method (FIG. 3A).

Then, an oxynitride film 3 is formed by nitrifying the silicon oxide film 2 by use of  $\text{NH}_3$  gas and then oxidizing the same (FIG. 3B). The oxynitride film 3

acts as a first gate insulating film and is generally called a tunnel oxide film.

5       Next, a polysilicon film 4 with a film thickness of 200 nm having phosphor doped therein as impurity is formed on the oxynitride film 3 by use of the LPCVD method. The polysilicon film 4 is used as a first gate electrode. Generally, the polysilicon film 4 is called a floating gate. Then, a second gate insulating film 5 with a film thickness of 120 nm is formed on the floating gate 4 by use of the LPCVD method. After this, a polysilicon film 6 having phosphor doped therein as impurity is formed on the second insulating film 5 by use of the LPCVD method. The polysilicon film 6 is used as a second gate electrode and it is generally called a control gate. Then, an oxide film 7 is formed on the polysilicon film 6 by use of the LPCVD method (FIG. 3C).

10       Further, a photoresist 8 is coated on the oxide film 7 and the oxide film 7 is processed into a desired pattern by use of the photoetching method (FIG. 3D).

25       Next, the photoresist 8 is removed. The etching process is effected in a direction perpendicular to the main surface of the silicon substrate 1 by use of a dry etching method such as an RIE (Reactive Ion Etching) method with the patterned oxide film 7 used as a mask so as to sequentially form control gates 6, second gate insulating films 5 and floating gates 4 (FIG. 3E).

After the post oxidation film 9 is formed, impurity is doped into the silicon substrate 1 by an ion-implantation process with the stacked gate structures STG of the control gates 6 and floating gates 4 used as a mask so as to form source and drain regions 10 and then the doped impurity is activated by annealing to form cell transistors (FIG. 3G).

20                   However, since the nitrogen concentration in the  
tunnel oxide film is high if the oxynitride film 3 is  
used as the tunnel oxide film as described above, it  
becomes difficult to form the post oxidation film 9.  
Therefore, the damage caused in the tunnel oxide film 3  
25                   in the RIE process cannot be eliminated. Further, as  
shown by an enlarged portion in FIG. 4, the neighboring  
portion of the edge of the floating gate 4 is not

oxidized and is formed in a sharpened shape.

In a flash memory, a state in which electrons exist in the floating gate 4 corresponds to a programmed state "0" and a state in which electrons do not exist in the floating gate 4 corresponds to an erase state "1". Since electrons pass through the tunnel oxide film 3 in both directions to set up the programmed state and erase state, some electrons are trapped in the tunnel oxide film 3 to reduce a current amount if a damage D occurring in the RIE process is kept left in the tunnel oxide film 3. Further, if a portion of the floating gate 4 is not oxidized at the time of post oxidation and is left behind with the corner portion sharpened, an electric field is concentrated on the above portion and degradation of the tunnel oxide film 3 will occur more rapidly.

As described above, in the conventional semiconductor device manufacturing method, the damage of the gate insulating film 3 caused at the etching time of the control gates 6 and floating gates 4 cannot be eliminated if the thermal nitride film is used as the first insulating film and there occurs a problem that electrons are trapped in the gate insulating film 3 to reduce a current amount and an electric field is concentrated on part of the gate insulating film 3 to accelerate the degradation thereof.

BRIEF SUMMARY OF THE INVENTION

Accordingly, an object of this invention is to provide a semiconductor device manufacturing method capable of preventing that electrons are trapped in the gate insulating film to reduce a current amount and an electric field is concentrated on part of the gate insulating film to accelerate the degradation thereof by the presence of damage of the gate insulating film caused at the time of process of the gate electrode when the thermal nitride film is used as the gate insulating film.

Further, another object of this invention is to provide a semiconductor device manufacturing method capable of accelerating formation of an oxide film by the post oxidation process so as to enhance the performance of memory cells and MOS transistors and enhance the manufacturing yield and reliability of the semiconductor device.

The above object of this invention can be attained by a semiconductor device manufacturing method comprising the steps of forming a gate insulating film in an oxynitride form on the main surface of a semiconductor substrate; forming gate electrodes on the gate insulating film; forming impurity diffused layers on both sides of the respective gate electrodes in the semiconductor substrate; and removing part of the gate insulating film which lies on the impurity diffused

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layers.

According to the above manufacturing method, it becomes easier to form the post oxidation film since the gate insulating film which is formed in an oxynitride form on the impurity diffused layer is removed and it becomes possible to suppress an amount of electrons trapped in the gate insulating film since a damaged portion of the gate insulating film caused at the time of patterning of the gate electrodes is removed. Further, if the an insulating film is formed on the impurity diffused layer, the edge portion of the gate electrode can be rounded so as to suppress concentration of the electric field. Further, if an oxynitride film is formed on the impurity diffused layer, deterioration due to the heat treatment effected in the later step can be suppressed.

The above object of this invention can also be attained by a semiconductor device manufacturing method comprising the steps of forming a gate insulating film in an oxynitride form on the main surface of a semiconductor substrate; forming gate electrodes on the gate insulating film; forming impurity diffused layers on both sides of the respective gate electrodes in the semiconductor substrate; and making the nitrogen concentration of part of the gate insulating film which lies on the impurity diffused layers lower than the nitrogen concentration of part of the gate insulating



damage of the gate insulating film caused at the time of processing of the gate electrodes can be eliminated and an amount of electrons trapped in the gate insulating film can be reduced. Further, the edge portion of the gate electrode can be rounded so as to suppress concentration of the electric field. In addition, since the oxynitride film is formed on the impurity diffused layers, nitrogen is extracted from the edge portion of the gate electrode after the edge portion of the gate electrode is rounded so that nitrogen can be introduced into the gate electrode again so as to reduce an amount of electrons trapped in the gate insulating film.

The above object of this invention can also be attained by a semiconductor device manufacturing method comprising the steps of forming a first insulating film in an oxynitride form on the main surface of a semiconductor substrate; forming a first conductive layer on the first insulating film; forming a second insulating film on the first conductive layer; forming a second conductive layer on the second insulating film; forming a third insulating film on the second conductive layer; patterning the third insulating film to form a mask; etching the second conductive layer, second insulating film and first conductive layer with the patterned third insulating film used as a mask to form stacked gate structures each having a control gate,

second gate insulating film and floating gate; removing  
part of the first insulating film which lies on the  
main surface of the semiconductor substrate and is  
disposed between the stacked gate structures to expose  
5 the main surface of the semiconductor substrate and  
leave another part of the first insulating film under  
the stacked gate structures, each part of the first  
insulating film which is left behind under the stacked  
gate structures acting as a first gate insulating film;  
10 forming a fourth insulating film on the side walls and  
upper surfaces of the stacked gate structures and the  
exposed main surface of the semiconductor substrate;  
and doping impurity into the main surface of the  
semiconductor substrate with the stacked gate  
15 structures used as a mask to form source and drain  
regions.

According to the above manufacturing method, since  
the first gate insulating film which is formed in the  
oxynitride form on the source and drain regions is  
20 removed, it becomes easier to form the post oxidation  
film and it becomes possible to eliminate the damaged  
portion of the first gate insulating film caused at the  
time of patterning of the first, second gate electrodes,  
and therefore, an amount of electrons trapped in the  
25 first gate insulating film can be reduced. Further, if  
an insulating film is formed on the source and drain  
regions, the edge portion of the first gate electrode

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gate structures acting as a first gate insulating film;  
doping impurity into the main surface of the  
semiconductor substrate with the stacked gate  
structures used as a mask to form source and drain  
5 regions; and making the nitrogen concentration of part  
of the first gate insulating film which lies on the  
impurity diffused layers lower than the nitrogen  
concentration of part of the first gate insulating film  
which lies under the stacked gate structures by  
10 oxidizing the stacked gate structures and impurity  
diffused layers at temperatures not lower than 950°C.

According to the above manufacturing method, since  
the nitrogen concentration of part of the first gate  
insulating film which lies on the source and drain  
15 regions is made lower than the nitrogen concentration  
of part of the first gate insulating film which lies  
under the floating gates, it becomes easier to form the  
post oxidation film and it becomes possible to  
eliminate the damage of the first gate insulating film  
20 caused at the time of etching of the control gates and  
floating gates. As a result, an amount of electrons  
trapped in the first gate insulating film can be  
reduced. Further, the edge portion of the floating  
gate can be rounded so as to suppress concentration of  
25 the electric field.

Further, the above object of this invention can be  
attained by a semiconductor device manufacturing method

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comprising the steps of forming a first insulating film in an oxynitride form on the main surface of a semiconductor substrate; forming a first conductive layer on the first insulating film; forming a second insulating film on the first conductive layer; forming a second conductive layer on the second insulating film; forming a third insulating film on the second conductive layer; patterning the third insulating film to form a mask; etching the second conductive layer, second insulating film and first conductive layer with the patterned third insulating film used as a mask to form stacked gate structures each having a control gate, second gate insulating film and floating gate; removing part of the first insulating film on the main surface of the semiconductor substrate which lies between the stacked gate structures to expose the main surface of the semiconductor substrate and leave another part of the first insulating film under the stacked gate structures, each part of the first insulating film which is left behind under the stacked gate structures acting as a first gate insulating film; doping impurity into the main surface of the semiconductor substrate with the stacked gate structures used as a mask to form source and drain regions; forming a post oxidation film on the source and drain regions; and forming an oxynitride film on the post oxidation film.

According to the above manufacturing method, the

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## BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

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principles of the invention.

FIG. 1 is a pattern plan view showing the memory cell structure of a NAND cell type flash memory;

FIG. 2 is an equivalent circuit diagram of a  
5 memory cell in a NAND cell type flash memory;

FIGS. 3A to 3G are cross sectional views sequentially showing the manufacturing steps of cell transistors in the NAND cell type flash memory, for illustrating a conventional method for manufacturing a  
10 semiconductor device;

FIG. 4 is a cross sectional view showing an enlarged portion of a neighboring portion of the floating gate in the cell transistor in a case where the cell transistor is formed by use of the  
15 conventional manufacturing process;

FIGS. 5A to 5H are cross sectional views sequentially showing the manufacturing steps of cell transistors in a NAND cell type flash memory, for illustrating a method for manufacturing semiconductor  
20 devices according to a first embodiment of this invention;

FIG. 6 is a cross sectional view showing an enlarged portion of a neighboring portion of the floating gate in the cell transistor in a case where the cell transistor is formed by use of the  
25 manufacturing process according to this invention;

FIGS. 7A to 7I are cross sectional views

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sequentially showing the manufacturing steps of cell transistors in a NAND cell type flash memory, for illustrating a method for manufacturing semiconductor devices according to a second embodiment of this invention;

FIGS. 8A to 8G are cross sectional views sequentially showing the manufacturing steps of cell transistors in a NAND cell type flash memory, for illustrating a method for manufacturing semiconductor devices according to a third embodiment of this invention;

FIG. 9 is a diagram showing the relation between a nitrogen extraction amount in an oxynitride film and an oxidation method;

FIGS. 10A to 10H are cross sectional views sequentially showing the manufacturing steps of cell transistors in a NAND cell type flash memory, for illustrating a method for manufacturing semiconductor devices according to a fourth embodiment of this invention; and

FIG. 11 is a cross sectional view showing a part of the manufacturing steps of cell transistor in a NAND cell type flash memory, for illustrating a method for manufacturing semiconductor devices according to a modification of this invention.

DETAILED DESCRIPTION OF THE INVENTION

[First Embodiment]

FIGS. 5A to 5G are cross sectional views partly  
and sequentially showing the manufacturing steps of a  
5 NAND cell type flash memory, for illustrating a method  
for manufacturing a semiconductor device according to a  
first embodiment of this invention and each corre-  
sponding to the cross section taken along the 3-3 line  
of the pattern plan view shown in FIG. 1.

10 In this embodiment, in a case where an oxynitride  
film is used as a gate insulating film of each cell  
transistor in a NAND cell type flash memory, the  
oxynitride film is removed after electrodes (control  
gates and floating gates) are processed, and then, a  
15 post oxidation film is formed.

First, a silicon oxide film 12 with a film  
thickness of 7 nm, for example, is formed on a silicon  
substrate (semiconductor substrate) 11 by use of the  
thermal oxidation method (FIG. 5A).

20 Then, an oxynitride film 13 is formed by  
nitrifying the silicon oxide film 12 by use of  $\text{NH}_3$  gas  
and then oxidizing the same (FIG. 5B). The oxynitride  
film 13 acts as a first gate insulating film and is  
generally called a tunnel oxide film.

25 Next, a polysilicon film 14 with a film thickness  
of 200 nm having phosphor doped therein as impurity is  
formed on the oxynitride film 13 by use of the LPCVD

method. The polysilicon film 14 is used as a first gate electrode. Generally, the polysilicon film 14 is called a floating gate. Then, a second gate insulating film 15 with a film thickness of 120 nm is formed on the polysilicon film 14 by use of the LPCVD method. As the second gate insulating film 15, for example, a single-layered silicon oxide film, a so-called ONO structure having a silicon oxide film and silicon nitride film stacked on each other, or an ONO structure having a silicon oxide film, silicon nitride film and silicon oxide film stacked on each other can be used. After this, a polysilicon film 16 having phosphor doped therein as impurity is formed on the second gate insulating film 15 by use of the LPCVD method. The polysilicon film 16 is used as a second gate electrode and generally called a control gate. Then, an oxide film 17 is formed on the polysilicon film 16 by use of the LPCVD method (FIG. 5C).

Further, a photoresist 18 is coated on the oxide film 17 and the oxide film 17 is processed into a desired pattern by use of the photoetching method (FIG. 5D).

Next, the photoresist 18 is removed. The etching process is effected in a direction perpendicular to the main surface of the silicon substrate 11 by use of a dry etching method such as an RIE (Reactive Ion Etching) method with the patterned oxide film 17 used

After this, a film with high nitrogen concentration is selectively etched by use of hot phosphoric acid (FIG. 5F). As a result, the oxynitride film 13 is removed except a portion which lies under the floating gates 14 so as to expose the main surface of the silicon substrate 11.

15           After the post oxidation films 19 are formed, in  
order to form source and drain regions 20, impurity is  
ion-implanted into the silicon substrate 11 with the  
stacked gate structures STG used as a mask and ion-  
implanted ions are activated by annealing to form cell  
20 transistors (FIG. 5H).

In this embodiment, since the oxynitride film 13 on the source and drain regions (impurity diffused layers) 20 is removed by etching, it becomes easier to form the post oxidation film. As a result, the damage of the gate insulating film 13 caused at the time of processing (etching) of the electrodes such as the control gates 16 and floating gates 14 can be

eliminated and an amount of electrons trapped in the gate insulating film 13 can be reduced. As shown in FIG. 6, since an edge portion 14A of the floating gate 14 used as a first gate electrode which lies on the tunnel oxide film (oxynitride film 13) side can be rounded, concentration of the electric field can be suppressed.

Further, in this embodiment, hot phosphoric acid is used to remove the oxynitride film 13, but this is not limitative, and a mixed solution of hydrofluoric acid and glycerol, a mixed solution of hydrofluoric acid and ethylene glycol, a mixed solution of hydrofluoric acid and ethylene glycol mono-ethyl ether or hydrofluoric acid vapor may be used to remove the oxynitride film 13. Further, the oxynitride film 13 can be etched and removed by isotropic etching such as CDE (Chemical Dry Etching) and if the post oxidation film 19 is formed by use of a wet oxidation process, the same effect can be attained.

[Second Embodiment]

FIGS. 7A to 7I are cross sectional views partly and sequentially showing the manufacturing steps of a NAND cell type flash memory, for illustrating a method for manufacturing a semiconductor device according to a second embodiment of this invention and each corresponding to the cross section taken along the 3-3 line of the pattern plan view shown in FIG. 1.

In this embodiment, in a case where an oxynitride film is used as a gate insulating film of each cell transistor in a NAND cell type flash memory, the oxynitride film is removed after electrodes (control gates and floating gates) are processed, then an oxide film is newly formed, and after this, the oxide film is nitrified by use of  $\text{NH}_3$  gas and then oxidized again to form an oxynitride film.

First, a silicon oxide film 12 with a film thickness of 7 nm, for example, is formed on a silicon substrate 11 by use of the thermal oxidation method (FIG. 7A).

Then, an oxynitride film 13 is formed by nitrifying the silicon oxide film 12 by use of  $\text{NH}_3$  gas and then oxidizing the same (FIG. 7B). The oxynitride film 13 acts as a first gate insulating film (tunnel oxide film).

Next, a polysilicon film 14 with a film thickness of 200 nm having phosphor doped therein as impurity is formed on the oxynitride film 13 by use of the LPCVD method. The polysilicon film 14 is used as a first gate electrode (floating gate). Then, a second gate insulating film 15 with a film thickness of 120 nm is formed on the polysilicon film 14 by use of the LPCVD method. As the second gate insulating film 15, for example, a single-layered silicon oxide film, a so-called ON structure having a silicon oxide film and

silicon nitride film stacked on each other, or an ONO structure having a silicon oxide film, silicon nitride film and silicon oxide film stacked on each other can be used. After this, a polysilicon film 16 having phosphor added therein as impurity is formed on the second gate insulating film 15 by use of the LPCVD method. The polysilicon film 16 is used as a second gate electrode (control gate). Then, an oxide film 17 is formed on the polysilicon film 16 by use of the LPCVD method (FIG. 7C).

Further, a photoresist 18 is coated on the oxide film 17 and the oxide film 17 is processed into a desired pattern by use of the photoetching method (FIG. 7D).

Next, the photoresist 18 is removed. The etching process is effected in a direction perpendicular to the main surface of the silicon substrate 11 by use of a dry etching method such as an RIE (Reactive Ion Etching) method with the patterned oxide film 17 used as a mask so as to sequentially form control gates 16, second gate insulating films 15 and floating gates 14 (FIG. 7E).

After this, a film with high nitrogen concentration is selectively etched by use of hot phosphoric acid (FIG. 7F). As a result, the oxynitride film 13 is removed except a portion thereof which lies under the floating gates 14 so as to expose the main

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surface of the silicon substrate 11.

Then, silicon oxide films (post oxidation films) 19 are formed on the exposed main surface of the silicon substrate 11 and the side walls and upper surfaces of the stacked gate structures STG by use of the thermal oxidation method (FIG. 7G).

After this, the post oxidation films 19 are nitrified by use of  $\text{NH}_3$  gas and then oxidized again to form oxynitride films 19' (FIG. 7H).

Then, in order to form source and drain regions 20, impurity is ion-implanted into the silicon substrate 11 with the stacked gate structures STG used as a mask and ion-implanted ions are activated by annealing to form cell transistors (FIG. 7I).

In this embodiment, since the oxynitride film 13 is removed by etching, it becomes easier to form the post oxidation film and a portion of the gate insulating film 13 which is damaged at the time of processing of the electrodes such as the control gates 16 and floating gates 14 can be restored. Further, as shown in FIG. 6, since an edge portion 14A of the floating gate 14 used as a first gate electrode which lies on the tunnel oxide film (oxynitride film 13) side can be rounded, concentration of the electric field can be suppressed. In addition, since the post oxidation film 19 is formed into an oxynitride form, deterioration of the gate insulating film caused by the

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heat treatment process in the later step can be suppressed.

Like the first embodiment, in this embodiment, hot phosphoric acid is used to remove the oxynitride film 13, but this is not limitative, and a mixed solution of hydrofluoric acid and glycerol, a mixed solution of hydrofluoric acid and ethylene glycol, a mixed solution of hydrofluoric acid and ethylene glycol mono-ethyl ether or hydrofluoric acid vapor may be used to remove the oxynitride film 13. Further, the oxynitride film 13 can be etched and removed by isotropic etching such as CDE and if the post oxidation film 19 is formed by use of a wet oxidation process, the same effect can be attained.

[Third Embodiment]

FIGS. 8A to 8G are cross sectional views partly and sequentially showing the manufacturing steps of a NAND cell type flash memory, for illustrating a method for manufacturing a semiconductor device according to a third embodiment of this invention and each corresponding to the cross section taken along the 3-3 line of the pattern plan view shown in FIG. 1.

In this embodiment, in a case where an oxynitride film is used as a gate insulating film of each cell transistor in a NAND cell type flash memory, the post oxidation process after processing electrodes (control gates and floating gates) is effected by a

high-temperature wet etching process.

First, a silicon oxide film 12 with a film thickness of 7 nm, for example, is formed on a silicon substrate 11 by use of the thermal oxidation method (FIG. 8A).

Then, an oxynitride film 13 is formed by nitrifying the silicon oxide film 12 by use of  $\text{NH}_3$  gas, NO gas or  $\text{N}_2\text{O}$  gas and then oxidizing the same (FIG. 8B). The oxynitride film 13 acts as a first gate insulating film (tunnel oxide film).

Next, a polysilicon film 14 with a film thickness of 200 nm having phosphor doped therein as impurity is formed on the oxynitride film 13 by use of the LPCVD method. The polysilicon film 14 is used as a first gate electrode (floating gate). Then, a second gate insulating film 15 with a film thickness of 120 nm is formed on the polysilicon film 14 by use of the LPCVD method. As the second gate insulating film 15, for example, a single-layered silicon oxide film, a so-called ON structure having a silicon oxide film and silicon nitride film stacked on each other, or an ONO structure having a silicon oxide film, silicon nitride film and silicon oxide film stacked on each other can be used. After this, a polysilicon film 16 having phosphor doped therein as impurity is formed on the second gate insulating film 15 by use of the LPCVD method. The polysilicon film 16 is used as a second

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gate electrode (control gate). Then, an oxide film 17 is formed on the polysilicon film 16 by use of the LPCVD method (FIG. 8C).

5 After this, a photoresist 18 is coated on the oxide film 17 and the oxide film 17 is processed into a desired pattern by use of the photoetching method (FIG. 8D).

10 Next, the photoresist 18 is removed. The etching process is effected in a direction perpendicular to the main surface of the silicon substrate 11 by use of a dry etching method such as an RIE (Reactive Ion Etching) method with the patterned oxide film 17 used as a mask so as to sequentially form control gates 16, second gate insulating films 15 and floating gates 14 (FIG. 8E).

15 After this, silicon oxide films (post oxidation films) 19 are formed by use of a high-temperature wet etching process (FIG. 8F). At the time of formation of the silicon oxide films 19, nitrogen is extracted from part of the oxynitride film 13 which is not covered with the floating gate 14 and the nitrogen concentration of the above part is lowered.

20 After the post oxidation films 19 are formed, impurity is ion-implanted into the silicon substrate 11 with the stacked gate structures STG used as a mask so as to form source and drain regions 20 and ion-implanted ions are activated by annealing to form cell

transistors (FIG. 8G).

In this embodiment, since the nitrogen concentration of part of the oxynitride film 13 which lies on the source and drain regions 20 and is not covered with the floating gates 14 is lowered at the time of formation of the silicon oxide films 19, it becomes easier to form the post oxidation films 19. As a result, the damage portion of the gate insulating film (oxynitride film) 13 caused at the time of etching of the control gates 16 and floating gates 14 can be eliminated and an amount of electrons trapped in the gate insulating film 13 can be reduced. Further, as shown in FIG. 6, since an edge portion 14A of the floating gate 14 (first gate electrode) which lies on the tunnel oxide film 13 side can be rounded, concentration of the electric field can be suppressed.

Further, in this embodiment, the post oxidation film 13 is formed by use of the wet etching process, but the oxidation temperature used at this time may be preferably set in a range of 950°C to 1190°C and if the above condition is satisfied, the effect that nitrogen in the oxynitride film 13 can be extracted by approx. 30% can be attained.

FIG. 9 shows the relation between an extraction amount of nitrogen in the oxynitride film 13 and an oxidation method. As is clearly seen from FIG. 9, the nitrogen extraction rate is higher in the wet oxidation

process than in the dry O<sub>2</sub> oxidation process, and the nitrogen extraction amount becomes larger with a rise in the oxidation temperature in the wet oxidation process. If the oxidation temperature exceeds 950°C, it becomes possible to extract nitrogen in the oxynitride film 13 by approx. 30%. Preferably, the nitrogen concentration of the oxynitride film 13 is  $3 \times 10^{15}$  atoms/cm<sup>2</sup> or less.

[Fourth Embodiment]

FIGS. 10A to 10H are cross sectional views partly and sequentially showing the manufacturing steps of a NAND cell type flash memory, for illustrating a method for manufacturing a semiconductor device according to a fourth embodiment of this invention and each corresponding to the cross section taken along the 3-3 line of the pattern plan view shown in FIG. 1.

In this embodiment, in a case where an oxynitride film is used as a gate insulating film of each cell transistor in a NAND cell type flash memory, after a post oxidation film is formed, oxynitrifying the post oxidation film by use of NH<sub>3</sub> gas, NO gas or N<sub>2</sub>O gas. Thereafter, oxidizing the oxynitride film.

First, a silicon oxide film 12 with a film thickness of 7 nm, for example, is formed on a silicon substrate 11 by use of the thermal oxidation method (FIG. 10A).

Then, an oxynitride film 13 is formed by

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nitrifying the silicon oxide film 12 by use of  $\text{NH}_3$  gas, NO gas or  $\text{N}_2\text{O}$  gas and then oxidizing the same (FIG. 10B). The oxynitride film 13 acts as a first gate insulating film (tunnel oxide film).

5       Next, a polysilicon film 14 with a film thickness of 200 nm having phosphor doped therein as impurity is formed on the oxynitride film 13 by use of the LPCVD method. The polysilicon film 14 is used as a first gate electrode (floating gate). Then, a second gate  
10       insulating film 15 with a film thickness of 120 nm is formed on the polysilicon film 14 by use of the LPCVD method. As the second gate insulating film 15, for example, a single-layered silicon oxide film, a so-called ON structure having a silicon oxide film and  
15       silicon nitride film stacked on each other, or an ONO structure having a silicon oxide film, silicon nitride film and silicon oxide film stacked on each other can be used. After this, a polysilicon film 16 having phosphor doped therein as impurity is formed on the  
20       second gate insulating film 15 by use of the LPCVD method. The polysilicon film 16 is used as a second gate electrode (control gate). Then, an oxide film 17 is formed on the polysilicon film 16 by use of the LPCVD method (FIG. 10C).

25       After this, a photoresist 18 is coated on the oxide film 17 and the oxide film 17 is processed into a desired pattern by use of the photoetching method

(FIG. 10D).

Next, the photoresist 18 is removed. The etching process is effected in a direction perpendicular to the main surface of the silicon substrate 11 by use of a dry etching method such as an RIE (Reactive Ion Etching) method with the patterned oxide film 17 used as a mask so as to sequentially form control gates 16, second gate insulating films 15 and floating gates 14 (FIG. 10E).

After this, silicon oxide films (post oxidation films) 19 are formed by use of an oxyhydrogen combustion method using an external combustion equipment or vaporizer method using  $H_2O$  as an oxidizer (FIG. 10F).

After the post oxidation films 19 are formed, the oxide films 19 are nitrified by use of  $NH_3$  gas,  $NO$  gas or  $N_2O$  gas to form oxynitride films 19' (FIG. 10G).

After this, impurity is ion-implanted into the silicon substrate 11 with the stacked gate structures STG used as a mask in order to form source and drain regions 20 and ion-implanted ions are activated by annealing to form cell transistors (FIG. 10H).

In this embodiment, since nitrogen can be extracted from part of the post oxidation films 19' near the edge portion 14A after the shape of the edge portion 14A of the floating gate 14 is improved by forming the post oxidation film 19 into an oxynitride



form, nitrogen can be introduced again so as to reduce an amount of electrons trapped in the gate insulating film 13.

In the above fourth embodiment, a case where the post oxidation film 19 is formed by use of an oxyhydrogen combustion method using external combustion equipment or vaporizer method using H<sub>2</sub>O as an oxidizer is taken as an example is explained, but it is possible to use the wet oxidation process.

[Modification]

In the first to fourth embodiments, a case wherein the manufacturing process of the NAND cell type flash memory is taken as an example is explained, but it is of course possible to apply this invention to a manufacturing method of other semiconductor devices such as MOS transistors in the same manner as described above.

Further, after forming the stacked gate structure STG etched by the polysilicon film 16, the second gate insulating film 15 and the polysilicon film 14, end portions of the stacked gate structure STG are etched back by isotropic etching such as CDE (Chemical Dry Etching), then the end portions of the floating gate can be shift on to a no damage portion of the gate insulation film (tunnel oxidation film) as shown by a broken line in FIG. 11. Therefore, the damage caused in the gate insulating film (tunnel oxide film) 13 in

the RIE process can be eliminated, and reduce the influence of the element characteristics.

As described above, according to this invention, it is possible to provide a semiconductor device manufacturing method capable of preventing that electrons are trapped in the gate insulating film to reduce a current amount or the electric field is concentrated on part of the gate insulating film to accelerate deterioration thereof by the presence of damage of the gate insulating film caused at the time of processing of the gate electrodes in a case where a thermal nitride film is used as the gate insulating film.

Further, it is possible to provide a semiconductor device manufacturing method in which formation of the oxide film by the post heat treatment can be accelerated, the performances of memory cells or MOS transistors can be enhanced and the manufacturing yield and reliability can be enhanced.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

WHAT IS CLAIMED IS:

1. A semiconductor device manufacturing method comprising the steps of:

forming a gate insulating film in an oxynitride  
5 form on a main surface of a semiconductor substrate;  
forming gate electrodes on the gate insulating  
film;

forming impurity diffused layers on both sides of  
the respective gate electrodes in the semiconductor  
10 substrate; and

removing part of the gate insulating film which  
lies on the impurity diffused layers.

2. The semiconductor device manufacturing method  
according to claim 1, wherein said step of forming the  
15 gate insulating film includes steps of thermally  
oxidizing the main surface of the semiconductor  
substrate to form an oxide film, nitrifying the oxide  
film, and oxidizing the nitrified oxide film again.

3. The semiconductor device manufacturing method  
20 according to claim 1, wherein said step of removing  
part of the gate insulating film which lies on the  
impurity diffused layers is effected by using at least  
one of hot phosphoric acid, a mixed solution of  
hydrofluoric acid and glycerol, a mixed solution of  
25 hydrofluoric acid and ethylene glycol, a mixed solution  
of hydrofluoric acid and ethylene glycol mono-ethyl  
ether and hydrofluoric acid vapor.

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4. The semiconductor device manufacturing method according to claim 1, wherein said step of removing part of the gate insulating film which lies on the impurity diffused layers is effected by use of an isotropic etching process.

5. The semiconductor device manufacturing method according to claim 1, further comprising a step of forming an insulating film on the impurity diffused layers after said step of removing part of the gate insulating film which lies on the impurity diffused layers is effected.

6. The semiconductor device manufacturing method according to claim 5, wherein said step of forming an insulating film on the impurity diffused layers is forming a post oxidation film effected by use of thermal oxidation method.

7. The semiconductor device manufacturing method according to claim 6, further comprising a step of nitrifying the post oxidation film.

8. The semiconductor device manufacturing method according to claim 5, wherein said step of forming an insulating film on the impurity diffused layers is forming an oxidation film effected by using at least one of vaporizer method, an oxyhydrogen combustion method and wet oxidation method.

9. The semiconductor device manufacturing method according to claim 1, further comprising a step of

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forming an oxynitride film on the impurity diffused layers after said step of removing part of the gate insulating film which lies on the impurity diffused layers is effected.

- 5           10. A semiconductor device manufacturing method comprising the steps of:

          forming a gate insulating film in an oxynitride form on a main surface of a semiconductor substrate;

          forming gate electrodes on the gate insulating  
10       film;

          forming impurity diffused layers on both sides of the respective gate electrodes in the semiconductor substrate; and

          making nitrogen concentration of part of the gate  
15       insulating film which lies on the impurity diffused layers lower than nitrogen concentration of part of the gate insulating film which lies under the gate electrodes by oxidizing the gate electrodes and impurity diffused layers at temperatures not lower than  
20       950°C.

          11. The semiconductor device manufacturing method according to claim 10, wherein said step of lowering the nitrogen concentration of part of the gate insulating film which lies on the impurity diffused  
25       layers is effected by use of a wet oxidation method.

          12. A semiconductor device manufacturing method comprising the steps of:

forming a gate insulating film in an oxynitride form on a main surface of a semiconductor substrate; forming gate electrodes on the gate insulating film;

5 forming impurity diffused layers on both sides of the respective gate electrodes in the semiconductor substrate;

forming a post oxidation film on the impurity diffused layers; and

10 oxynitrifying the post oxidation film.

13. A semiconductor device manufacturing method comprising the steps of:

forming a first insulating film in an oxynitride form on a main surface of a semiconductor substrate;

15 forming a first conductive layer on the first insulating film;

forming a second insulating film on the first conductive layer;

20 forming a second conductive layer on the second insulating film;

forming a third insulating film on the second conductive layer;

patterning the third insulating film to form a mask;

25 etching the second conductive layer, second insulating film and first conductive layer with the third insulating film used as a mask to form stacked

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gate structures each having a control gate, second gate insulating film and floating gate;

removing part of the first insulating film which lies on the main surface of the semiconductor substrate and is disposed between the stacked gate structures to expose the main surface of the semiconductor substrate and leave another part of the first insulating film which lies under the stacked gate structures, each part of the first insulating film which is left behind under the stacked gate structures acting as a first gate insulating film;

forming a fourth insulating film on side walls and upper surfaces of the stacked gate structures and the exposed main surface of the semiconductor substrate; and

doping impurity into the main surface of the semiconductor substrate with the stacked gate structures used as a mask to form source and drain regions.

14. The semiconductor device manufacturing method according to claim 13, wherein said step of forming the first insulating film includes steps of thermally oxidizing the main surface of the semiconductor substrate to form an oxide film, nitrifying the oxide film, and oxidizing the nitrified oxide film again.

15. The semiconductor device manufacturing method according to claim 13, wherein said step of removing

part of the first insulating film is effected by using at least one of hot phosphoric acid, a mixed solution of hydrofluoric acid and glycerol, a mixed solution of hydrofluoric acid and ethylene glycol, a mixed solution of hydrofluoric acid and ethylene glycol mono-ethyl ether and hydrofluoric acid vapor.

16. The semiconductor device manufacturing method according to claim 13, wherein said step of removing part of the first insulating film which is effected by use of an isotropic etching process.

17. The semiconductor device manufacturing method according to claim 13, wherein said step of forming the fourth insulating film includes a step of forming oxide films on the side walls and upper surfaces of the stacked gate structures and the exposed main surface of the semiconductor substrate by use of a thermal oxidation method.

18. The semiconductor device manufacturing method according to claim 13, wherein said step of forming the fourth insulating film includes steps of forming oxide films on the side walls and upper surfaces of the stacked gate structures and the exposed main surface of the semiconductor substrate by use of a thermal oxidation method, nitrifying the oxide film, and oxidizing the nitrified oxide film again.

19. The semiconductor device manufacturing method according to claim 13, wherein said step of forming the



fourth insulating film includes a step of forming oxide films on the side walls and upper surfaces of the stacked gate structures and the exposed main surface of the semiconductor substrate by using at least one of  
5 vaporizer method, an oxyhydrogen combustion method and wet oxidation method.

20. A semiconductor device manufacturing method comprising the steps of:

forming a first insulating film in an oxynitride  
10 form on a main surface of a semiconductor substrate;  
forming a first conductive layer on the first insulating film;  
forming a second insulating film on the first conductive layer;  
15 forming a second conductive layer on the second insulating film;  
forming a third insulating film on the second conductive layer;  
patterning the third insulating film to form a  
20 mask;  
etching the second conductive layer, second insulating film and first conductive layer with the third insulating film used as a mask to form stacked gate structures each having a control gate, second gate  
25 insulating film and floating gate;  
removing part of the first insulating film which lies on the main surface of the semiconductor substrate

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and is disposed between the stacked gate structures to expose the main surface of the semiconductor substrate and leave another part of the first insulating film which lies under the stacked gate structures, each part  
5 of the first insulating film which is left behind under the stacked gate structures acting as a first gate insulating film;

doping impurity into the main surface of the semiconductor substrate with the stacked gate  
10 structures used as a mask to form source and drain regions; and

making nitrogen concentration of part of the first gate insulating film which lies on the impurity diffused layers lower than nitrogen concentration of  
15 part of the first gate insulating film which lies under the stacked gate structures by oxidizing the stacked gate structures and impurity diffused layers at temperatures not lower than 950°C.

21. The semiconductor device manufacturing method  
20 according to claim 20, wherein said step of lowering the nitrogen concentration of part of the gate insulating film which lies on the impurity diffused layers is effected by use of a wet oxidation method.

22. A semiconductor device manufacturing method  
25 comprising the steps of:

forming a first insulating film in an oxynitride form on a main surface of a semiconductor substrate;

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forming a first conductive layer on the first insulating film;

forming a second insulating film on the first conductive layer;

5        forming a second conductive layer on the second insulating film;

forming a third insulating film on the second conductive layer;

10        patterning the third insulating film to form a mask;

etching the second conductive layer, second insulating film and first conductive layer with the third insulating film used as a mask to form stacked gate structures each having a control gate, second gate  
15        insulating film and floating gate;

removing part of the first insulating film which lies on the main surface of the semiconductor substrate and is disposed between the stacked gate structures to expose the main surface of the semiconductor substrate  
20        and leave another part of the first insulating film under the stacked gate structures, each part of the first insulating film which is left behind under the stacked gate structures acting as a first gate insulating film;

25        forming a post oxidation film on side walls and upper surfaces of the stacked gate structures and the exposed main surface of the silicon substrate;

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oxynitrifying the post oxidation film; and  
doping impurity into the main surface of the  
semiconductor substrate with the stacked gate  
structures used as a mask to form source and drain  
regions.

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ABSTRACT OF THE DISCLOSURE

A thermal nitride film is formed as a gate  
insulating film on a silicon substrate, and after a  
gate electrode material is formed on the insulating  
5 film, it is patterned to form gate electrodes. After  
processing the electrodes, part of the gate insulating  
film other than a portion thereof which lies under the  
gate electrodes is removed. Further, an insulating  
film (a post oxidation film) is formed on side walls  
10 and upper surfaces of the stacked gate structures and  
the exposed main surface of the silicon substrate by  
use of thermal oxidation method.

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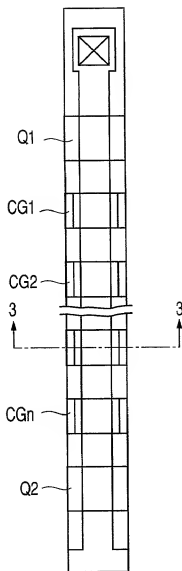


FIG. 1  
(PRIOR ART)

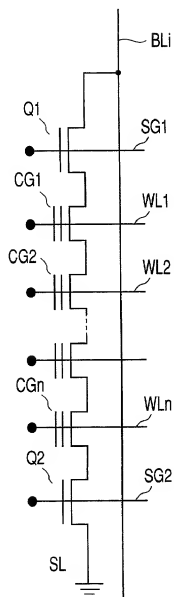


FIG. 2  
(PRIOR ART)

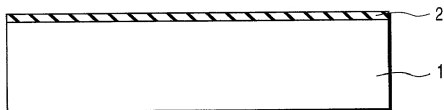


FIG. 3A (PRIOR ART)



FIG. 3B (PRIOR ART)

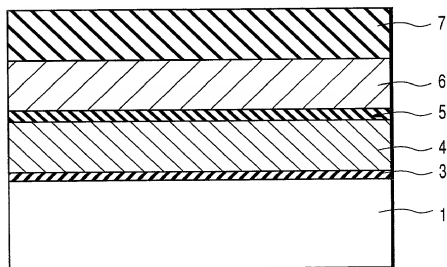


FIG. 3C (PRIOR ART)

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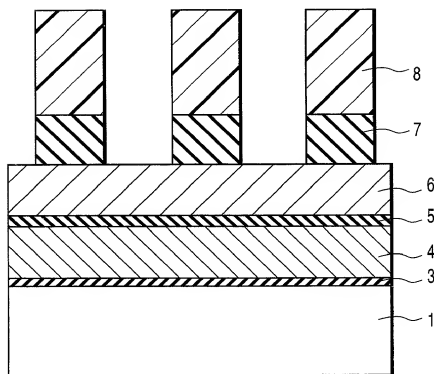


FIG. 3D (PRIOR ART)

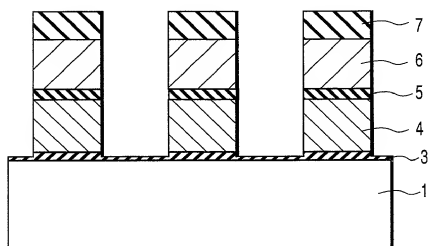


FIG. 3E (PRIOR ART)



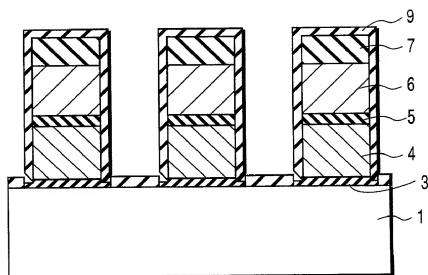


FIG. 3F (PRIOR ART)

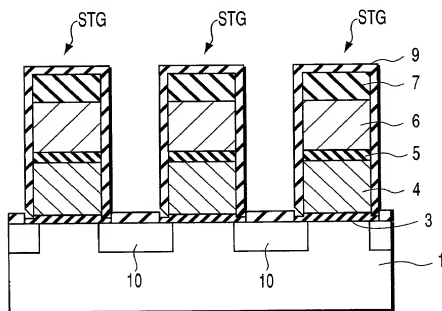


FIG. 3G (PRIOR ART)

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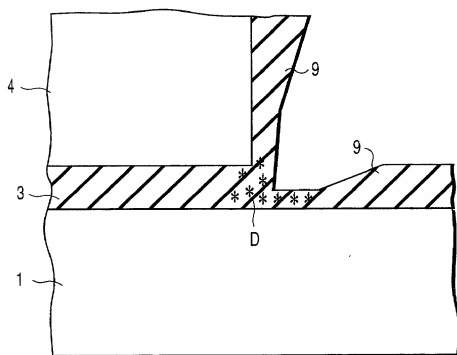


FIG. 4 (PRIOR ART)

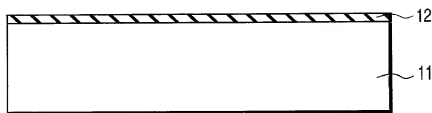


FIG. 5A



FIG. 5B

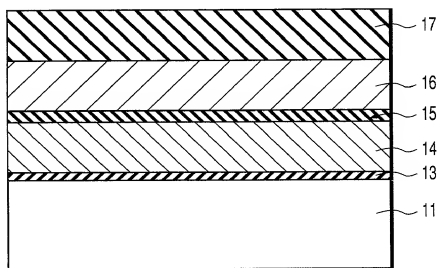


FIG. 5C

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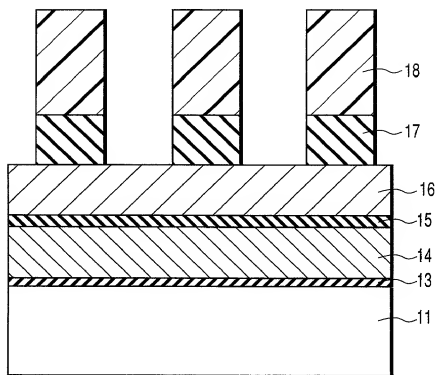


FIG. 5D

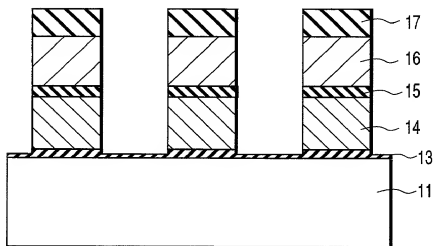


FIG. 5E

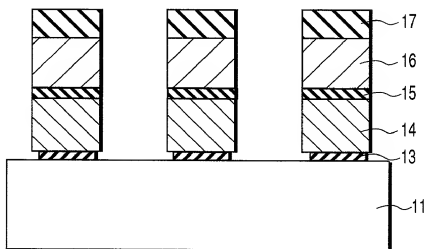


FIG. 5F

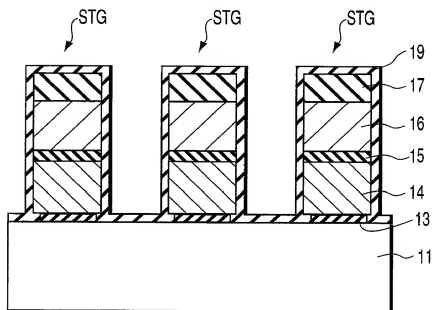


FIG. 5G

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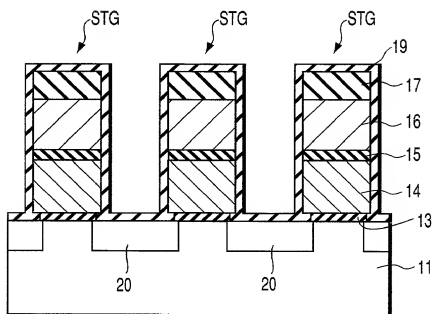


FIG. 5H

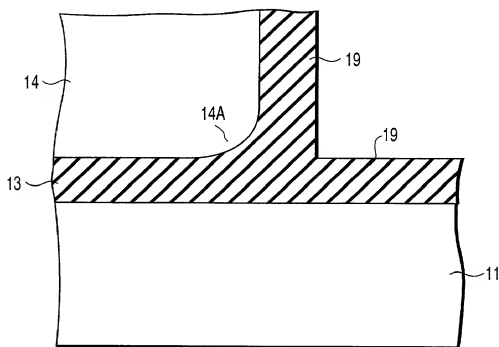


FIG. 6

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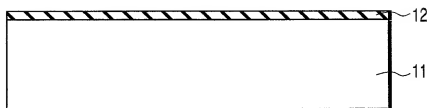


FIG. 7A

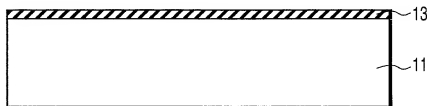


FIG. 7B

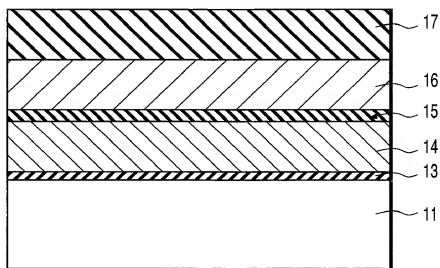


FIG. 7C

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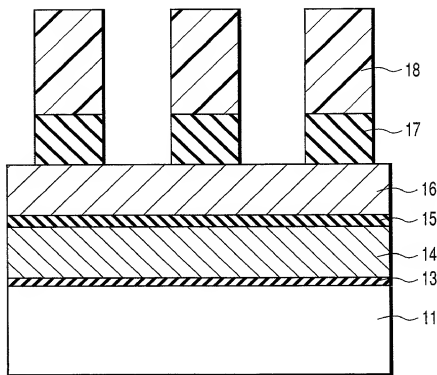


FIG. 7D

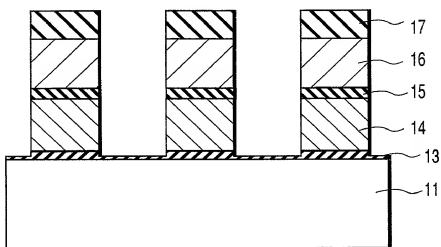


FIG. 7E



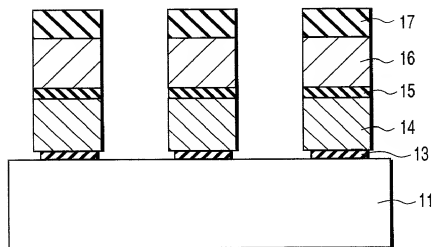


FIG. 7F

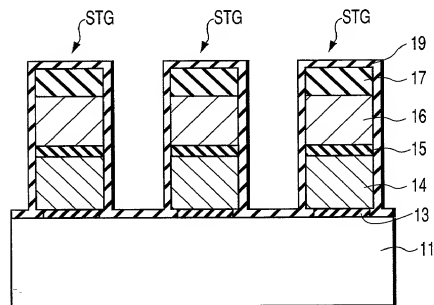


FIG. 7G

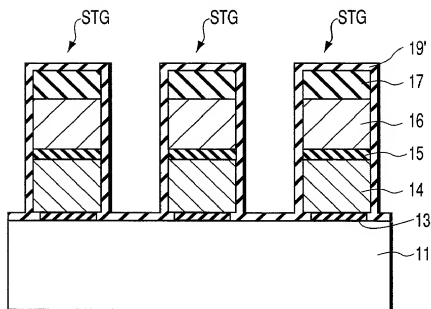


FIG. 7H

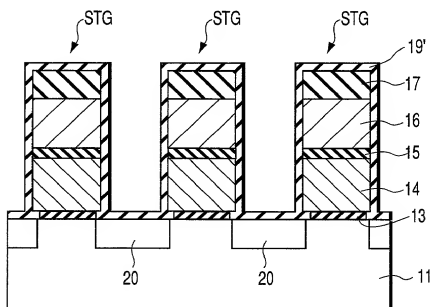


FIG. 7I

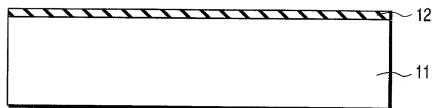


FIG. 8A



FIG. 8B

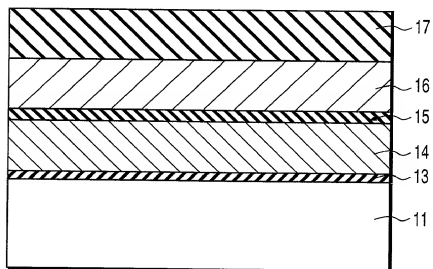


FIG. 8C

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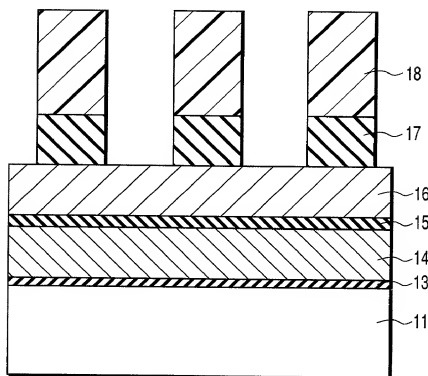


FIG. 8D

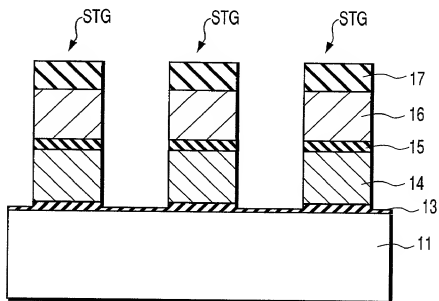


FIG. 8E

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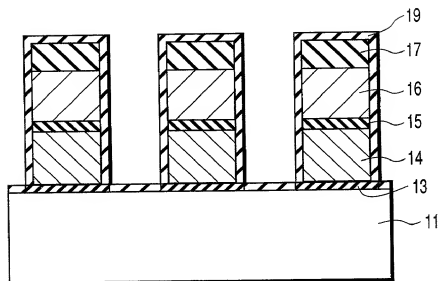


FIG. 8F

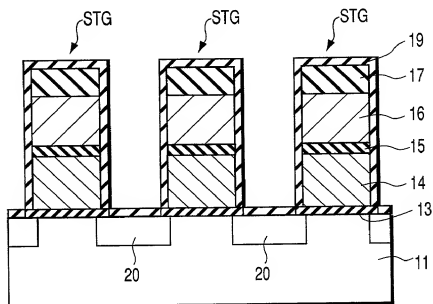


FIG. 8G

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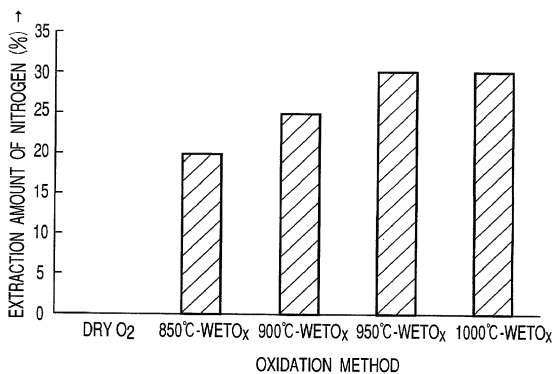


FIG. 9

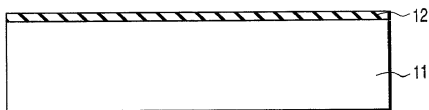


FIG. 10A



FIG. 10B

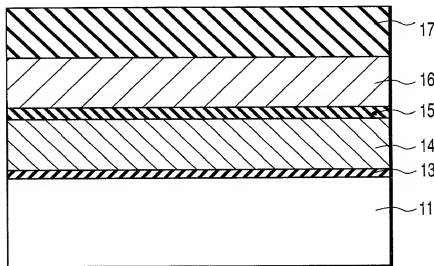


FIG. 10C

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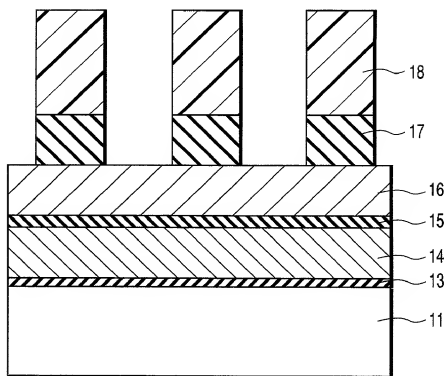


FIG. 10D

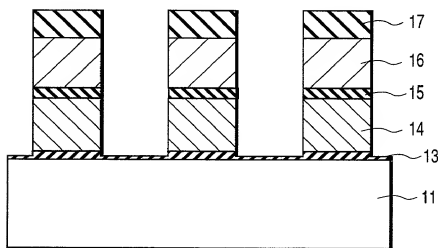


FIG. 10E



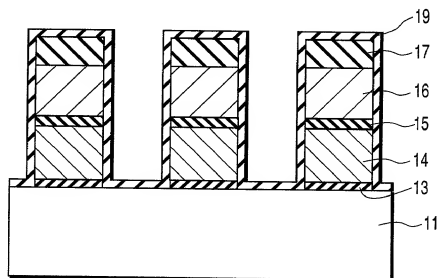


FIG. 10F

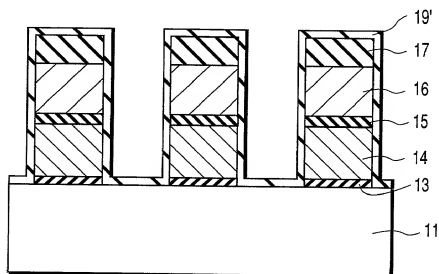


FIG. 10G

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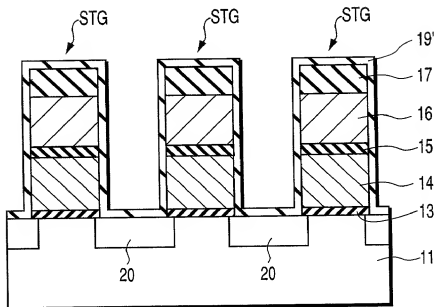


FIG. 10H

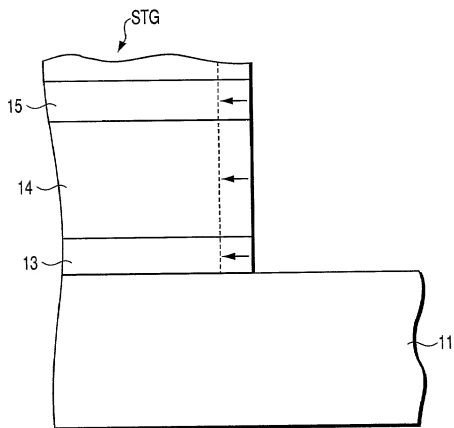


FIG. 11

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

IN RE APPLICATION OF: Wakako MORIYAMA, et al.

FILING DATE: Herewith

FOR: METHOD FOR MANUFACTURING SEMICONDUCTOR DEVICES USING THERMAL NITRIDE FILMS  
AS GATE INSULATING FILMS

**LIST OF INVENTORS' NAMES AND ADDRESSES**

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A declaration containing all the necessary information will be submitted at a later date.

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